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[54] **METHOD OF STRENGTHENING SILICON NITRIDE CERAMICS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 146,944, May 2, 1980, abandoned.

[51] Int. Cl.^{3} **B05D 3/02**
[52] U.S. Cl. **427/314;** 264/62; 427/193; 427/355; 427/399
[58] Field of Search 427/85, 93, 180, 193, 427/248.1, 255, 289, 443.2, 430.1, 397.7, 376.2, 376.4, 444, 314, 355, 399, 356; 106/73.2; 264/62

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[57] **ABSTRACT**

Si_3N_4 ceramics having a glassy phase densification aid are heated while their surface is in contact with SiO_2. The SiO_2 forms one side of a diffusion couple and draws the glassy phase out of the ceramic. The SiO_2 can be provided by heating the ceramic in air to form an SiO_2 scale by the oxidation of Si_3N_4, or by imbedding the ceramic in SiO_2 powder. Surface pits, if any, formed during oxidation, are removed by grinding.
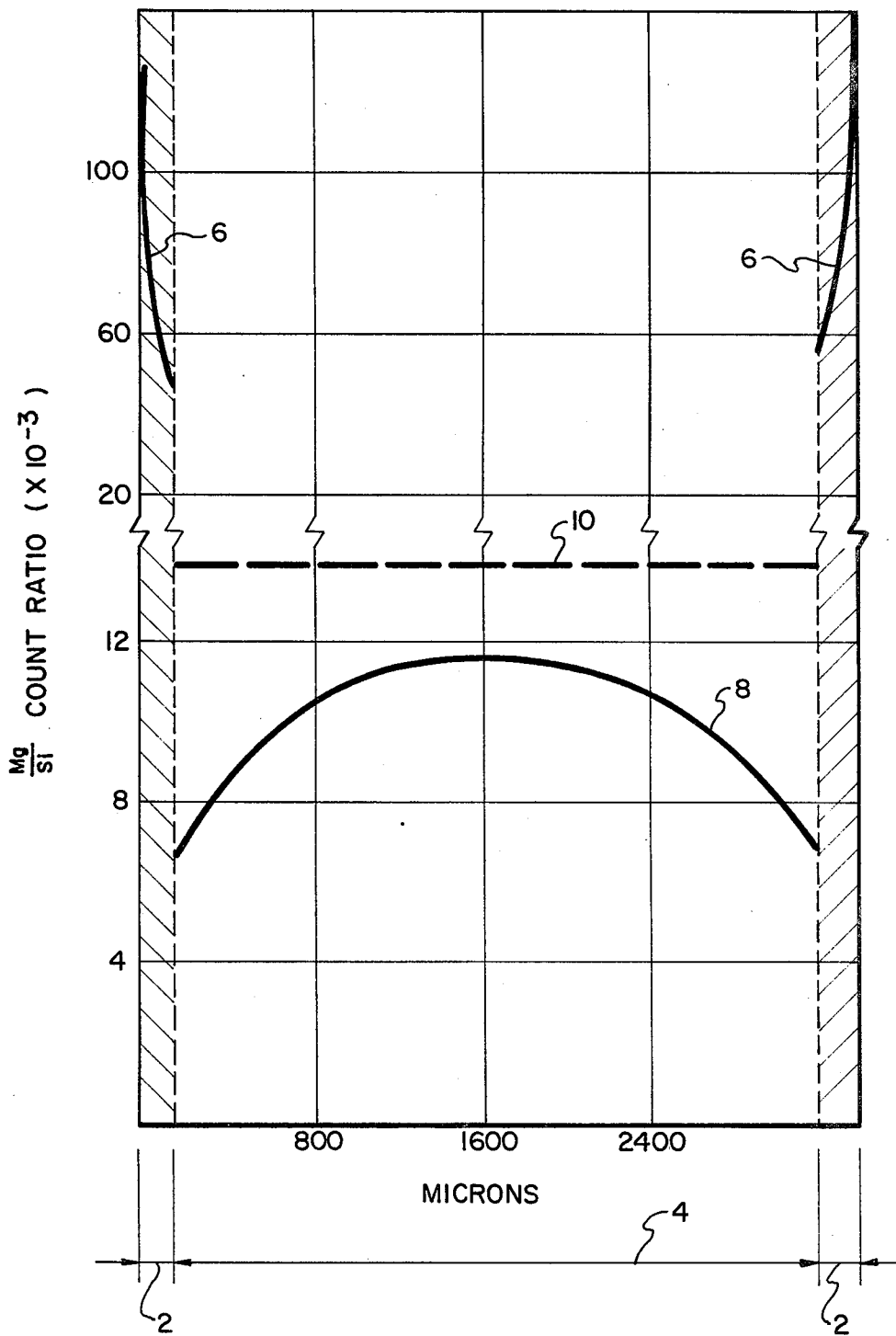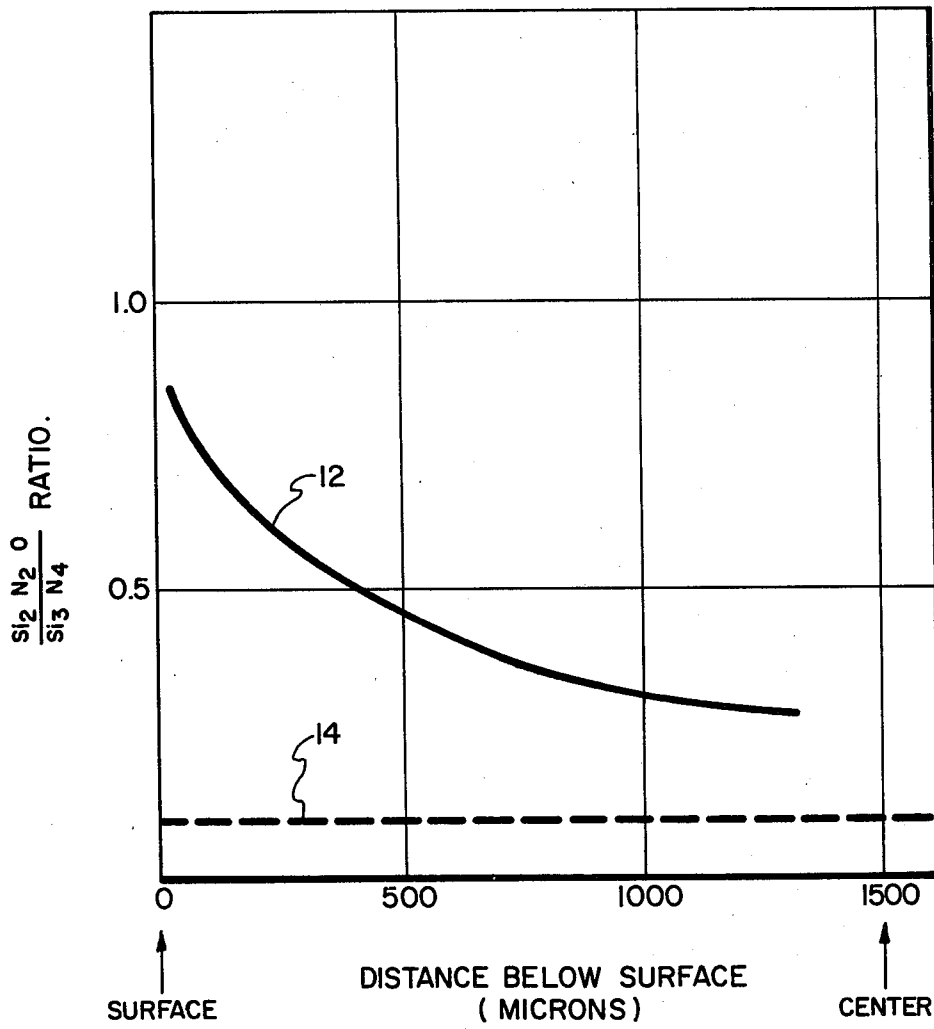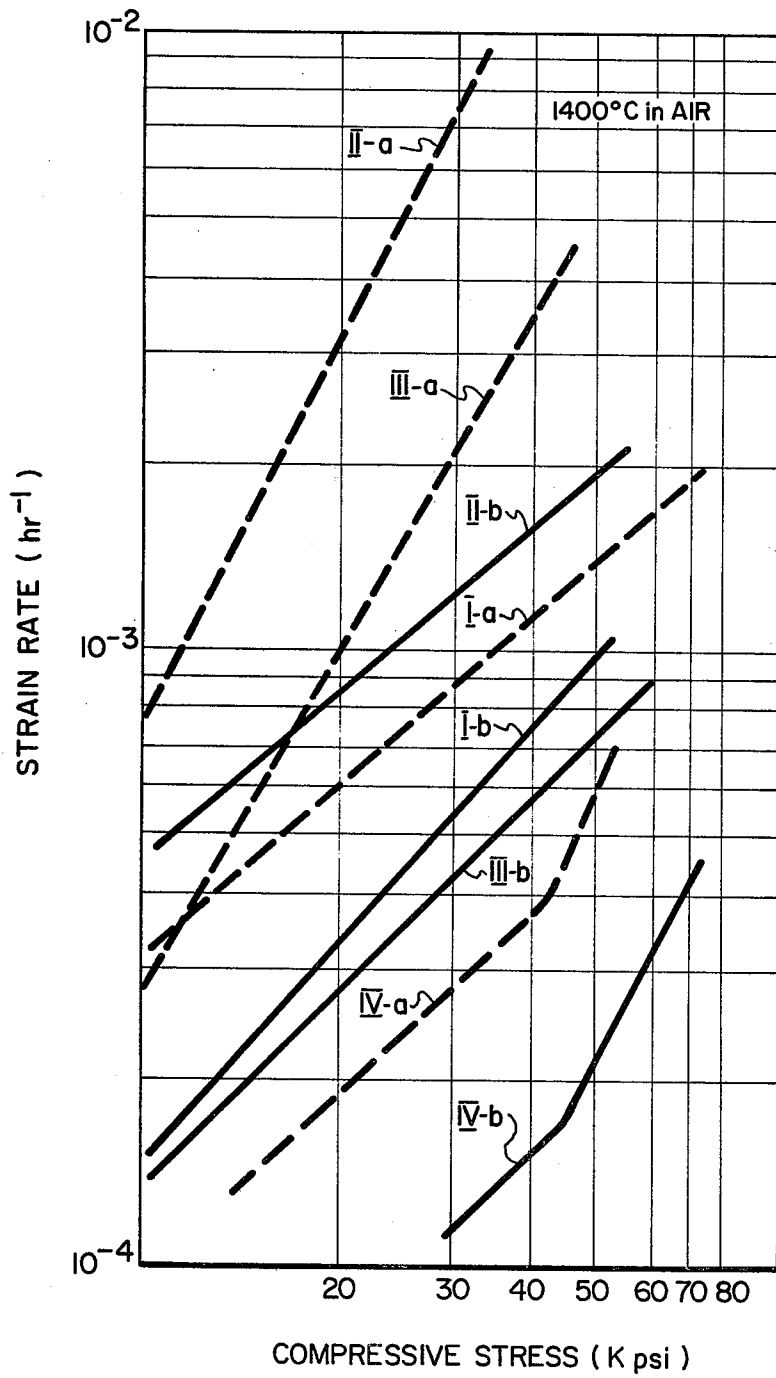
14 Claims, 3 Drawing Figures
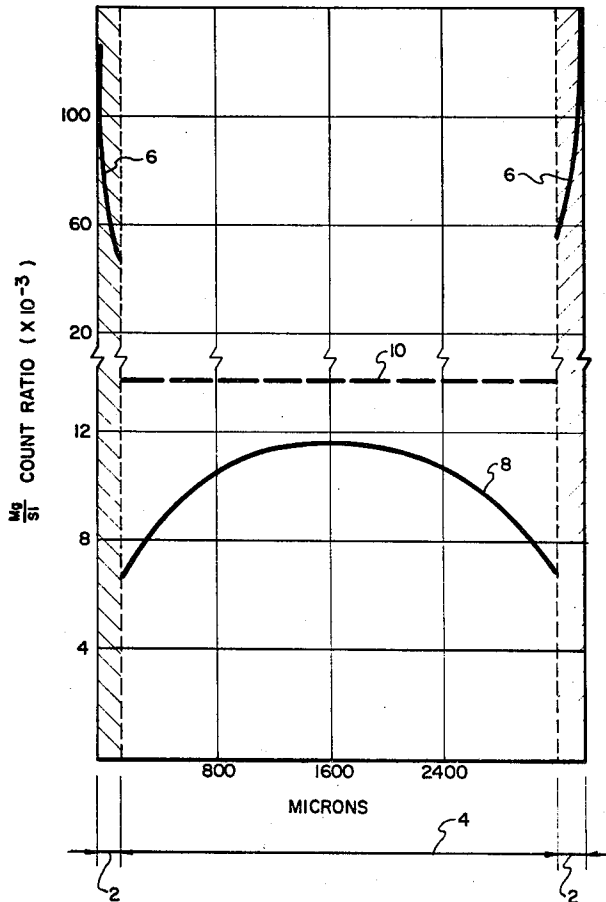
FIG.1.

FIG.2.

FIG.3.

METHOD OF STRENGTHENING SILICON NITRIDE CERAMICS

STATEMENT OF GOVERNMENT INTEREST

The invention described herein was made in the course of, or under a contract with the Air Force Office of Scientific Research.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 146,944, filed May 2, 1980, which is abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the field of ceramics and particularly to the field of silicon nitride (Si_3N_4) ceramics.

DESCRIPTION OF THE PRIOR ART

During the last decade, Si_3N_4 ceramics have received considerable attention primarily directed toward heat engine applications. Their intrinsic properties such as low thermal expansion and moderate elastic modulus minimize stresses developed during severe thermal transients better than other candidate structural ceramics. In practice, the chemical formula Si_3N_4 represents a family of ceramic materials in which Si_3N_4 constitutes the major phase.

Si_3N_4 ceramics are prepared by mixing Si_3N_4 powder with additive powders, and densifying the mixture by either hot-pressing or pressureless sintering. Hot pressing is usually carried out in graphite dies at temperatures between 1650° C. and 1750° C. for several hours under high pressures. Pressureless sintering is accomplished by forming the mixed powders into shapes before densification. These shaped, powdered parts are then sintered by heating them at the sintering temperature.

Si_3N_4 powder oxidizes when heated to high temperatures in air, and such oxidation is undesireable because it changes the composition of the powder, i.e., increases the SiO_2 content. Therefore, special precautions are taken during the processing and sintering of Si_3N_4 ceramic to prevent it from oxidizing. Such precautions include providing a protective atmosphere such as a nitrogen atmosphere, or packing the ceramic in a protective Si_3N_4 powder as described in U.S. Pat. No. 4,179,486 to Frederick F. Lange (one of the present inventors).

Additives, called densification aids, are required for densification, and these densification aids are mixed with Si_3N_4 powder. Current commercial, hot-pressed materials are fabricated using MgO as a densification aid. Other known densification aids include ZrO_2, Al_2O_3, BeO, and rare earth oxides such as Y_2O_3, CeO_2, Ce_2O_3, Nd_2O_3, and La_2O_3.

The densification aids react with Si_3N_4 and SiO_2 at high temperatures to form a liquid, which upon cooling results in a glassy phase located between the primary phase of crystalline Si_3N_4 grains so that the material is a dense, polyphase ceramic. Unfortunately, this glassy phase becomes viscous at high temperatures and causes the mechanical properties to degrade at high temperature. The temperature at which degradation begins depends on the composition of the glassy phase. The extent of degradation depends on the volume fraction of the glassy phase. Within a given system, compositions containing a smaller volume fraction of glassy phase have significantly higher strength and creep resistance at high temperature. However, compositions containing little or no glassy phase are difficult or impossible to densify.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an improved Si_3N_4 ceramic.

It is an object of the invention to provide a method of increasing the higher temperature strength of Si_3N_4 ceramics.

It is an objective of the invention to provide a method of fabricating a Si_3N_4 ceramic utilizing a densification aid to obtain rapid densification and still obtain a high strength Si_3N_4 ceramic.

It is an object of the invention to provide a method of reducing the amount of glassy phase in Si_3N_4 ceramics.

It is an objective of the invention to provide a method of increasing the oxidation resistance of Si_3N_4 ceramics.

According to the invention, silicon dioxide (SiO_2) is provided on the surface of a Si_3N_4 ceramic which has a glassy secondary phase located between grains and/or at grain triple junctions of the primary phase of crystalline Si_3N_4. The SiO_2 can be provided by immersing the Si_3N_4 alloy in powdered SiO_2, or by heating the Si_3N_4 alloy in air to oxidize the Si_3N_4 and form a thin scale of SiO_2.

The Si_3N_4 ceramic and the SiO_2 are then heated to a temperature which is sufficient to cause diffusion of cations from the silicates in the glassy phase into the SiO_2 scale or SiO_2 powder on the surface of the ceramic. This cation diffusion takes place because the SiO_2 on the surface forms a diffusion or reaction couple with the silicate glassy phase inside the ceramic. This outward cation diffusion and the inward diffusion of oxygen has been discovered to result in a change of both the chemistry and phase content of the bulk material. Any surface pits formed during the heating are removed by grinding.

High strength Si_3N_4 ceramics can be fabricated using sufficient quantities of densification aids to promote rapid densification during sintering despite the fact that the densification aids are known to decrease the high temperature strength of the ceramic. Then the high temperature strength of the ceramic can be improved by the oxidation-induced compositional changes procedures of the invention. This is possible because the compositional changes decrease the volume fraction of glassy phase.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a curve showing the distribution of Mg across the thickness (both scale and subscale) of an oxidized sample of an Si_3N_4-SiO_2-MgO ceramic;

FIG. 2 is a curve showing the oxidation of a Si_3N_4-SiO_2-MgO ceramic from its surface below the scale to its center plotted as a function of Si_2N_2O/Si_3N_4 ratio vs distance below the surface; and

FIG. 3 is a log-log plot of the strain rate vs compressive stress at 1400° C. for unoxidized and oxidized samples of Si_3N_4 ceramics.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Silicon nitride based ceramics are inherently unstable in oxidizing atmosphere, and since they are polyphase materials, their oxidation behavior is quite complex. Current commercial ceramics have a primary phase of Si_3N_4 grains and a glassy secondary phase used to densify the alloy. In the case of ceramics which use MgO as a densification aid (generally referred to a composition in the Si-Mg-O-N system), the glassy phase has a eutectic composition (in mole fraction) of approximately 0.1 Si_3N_4, 0.3 Si_2N_2O, and 0.6 Mg_2SiO_4. The glassy phase also contains small amounts of cation impurities such as Ca, Fe, Al, Mn, Na, and K. The glassy secondary phase is principally a continuous intergranular phase.

The oxidation of Si_3N_4 ceramics was investigated in work leading to the present invention. A variety of ceramics throughout the Si_3N_4-SiO_2-MgO system were investigated. These included two series containing 0.833 and 0.755 mole fraction of Si_3N_4. The materials were prepared by hot-pressing composite powders of Si_3N_4, MgO, and SiO_2 as known in the art. Specimens for oxidation were cut from each material and the constituent phases were identified by x-ray diffraction analysis. Specimens were then oxidized in air at 1400° C. in an open-ended furnace for 24 and 288 hours.

After oxidation, the specimens were cut in half. One half was used to determine the compositional gradient from the exterior to the interior. The procedure was to successively grind the surface and determine the surface phase with x-ray diffraction until the center of the specimen was reached. The other half was used for a non-dispersive x-ray microanalysis determination of the spatial distribution of elements from the oxidized surface to the interior. Samples having the same compsitions, but unoxidized, were sectioned and analyzed to provide calibrations for the x-ray microanalyses.

When the oxidized specimens were sectioned and polished, three distinct regions could be discerned in all the materials: a friable, white oxide scale, a sub-scale reaction zone beneath the scale and a central portion. For each specimen, it was found that the scale was greatly enriched in Mg and Ca relative to the unoxidized samples. There was no detectable enrichment or depletion of silicon in the material beneath the scale. In each of the specimens there was, however, a magnesium depletion in the subscale material, the extent of which was a function of the MgO/SiO_2 ratio of the starting composition. In the unoxidized samples, the Mg/Si ratio was independent of position, indicating that during oxidation, Mg had diffused to the scale from as far as the center of the specimens.

FIG. 1 shows the distribution of Mg in the scale 2 and in the sub-scale 4 based upon the Mg/Si ratios measured by x-ray microanalysis of a specimen having 0.755 mole fraction of Si_3N_4 which was oxidized for 288 hours at 1400° C. The specimen was 3360 microns thick and had developed a scale 180 microns thick on both exposed sides. The Mg/Si ratio in the sub-scale is shown in lower curve 8. THe ratio prior to oxidation is shown by dashed line 10. Since Mg is depleted in the immediate region below the scale, it appears that Mg is drawn into the scale faster than it diffuses from the interior into the scale.

Compositional changes within the sub-scale material were discovered after measuring the Si_2N_2O/Si_3N_4 ratio from the surface of the sub-scale material (just

under the scale) to the center of the specimen as shown by curve 12 in FIG. 2. Dashed line 14 shows the Si_2N_2O/Si_3N_4 ratio of the sample before oxidation. The decrease in Mg and the increase in Si_2N_2O shown in FIGS. 1 and 2 indicate that the glassy phase in the specimen has been reduced by the oxidation treatment, particularly near its surface.

The diffusion of Mg and cation impurities to the surface during oxidation is apparently caused by the formation of a reaction couple between the SiO_2 scale on the oxidized surface and the Mg containing glassy phase in the bulk of the material. This diffusion produces a compositional gradient and, thus, must produce a depletion gradient of the glassy phase. Since the composition at the scale/sub-scale interface has shifted furthest from the eutectic (or glass) composition, rules for interpreting phase diagrams indicate that the volume fraction of the glassy phase will be smallest at this interface. In terms of an equivalent phase diagram, the composition of the glassy phase is nearly identical to the eutectic composition and the composition in the subscale material has shifted away from the eutectic composition as a result of the compositional changes produced by diffusion.

The SiO_2 on the surface which forms one side of the diffusion couple and draws out the detrimental glassy phase can be provided simply by heating the specimen in air or oxygen as described above. This creates an SiO_2 scale on the oxidized surface as a result of the reaction of oxygen with Si_3N_4. In a second embodiment of the invention, the SiO_2 is provided by surrounding the Si_3N_4 ceramic with SiO_2 powder during a high temperature heat treatment. Cations (other than Si) which form the glassy phase will diffuse to the SiO_2 powder on the surface in an attempt to reach equilibrium.

The post-fabrication treatment methods of the invention will improve the high temperature stability of dense Si_3N_4 ceramics. Oxidation resistance is improved due to the decreased flux of anions (oxygen, nitrogen) and cations (additive and impurities) as the volume fraction of the glassy (or viscous) phase, which is the path for fast diffusion, is decreased by the post-fabrication treatment.

It has also been discovered that oxidation as described above increases the high temperature creep resistance and strength of Si_3N_4 ceramics. This is an important discovery because it makes Si_3N_4 ceramics more useful in structural applications. The strength increase is quite substantial, as shown by the following examples:

EXAMPLE I: Increased Creep Resistance

Specimens (approximately $0.3 \times 0.3 \times 0.9$ cm) were diamond cut from a ceramic of 0.75 mole fraction Si_3N_4, balance MgO and SiO_2, with a molar ratio of MgO/SiO_2 of 0.09. Some of the specimens were oxidized in an air furnace at 1400° C. for 100 hours. This created an oxide surface scale which was less than 50 μm thick.

Compressive creep testing was performed at 1400° C. in air on the unoxidized and on the oxidized specimens. Log-log plots of this data are shown in FIG. 3, dashed curve I-a being for the unoxidized specimen and solid curve I-b being for the oxidized specimen. As shown, the oxidation treatment greatly improved the compressive creep resistance.

EXAMPLE II: Increased Creep Resistance

Specimens were prepared as described for Example I except that the molar ratio of MgO/SiO_2 was 2.28. The compressive creep resistance is shown in FIG. 3, dashed curve II-a being for the unoxidized specimen and solid curve II-b being for the oxidized specimen. The creep strength of the oxidized specimen was considerably higher than the unoxidized specimen.

EXAMPLE III: Increased Creep Resistance

Specimens were prepared as described for Example I except that the mole fraction of Si_3N_4 was 0.83 and the molar ratio of MgO/SiO_2 was 2.40. The compressive creep resistance is shown in FIG. 3, dashed curve III-a being for the unoxidized specimen and solid curve III-b being for the oxidized specimen.

EXAMPLE IV: Increased Creep Resistance

To determine if the method applied to Si_3N_4 ceramics having a Y_2O_3 rather than MgO glass forming densifica-

The flexural strength at 1400° C. is shown in Table I for an unoxidized specimen and for a specimen oxidized in an air furnace at 1400° C. for 300 hours. The oxidized specimens had a significant increase in flexural strength.

EXAMPLE XX: Increased Strength

Flexural test specimens were diamond cut from a large billet of Si_3N_4 obtained from the Norton Company and commercially identified as NC-132 hot-pressed Si_3N_4. Specimens were subjected to oxidation in air at 1400° C. for 548 hours and then surface ground to remove pits as described for Examples V–XIX. The average flexural strength of the oxidized specimens at a test temperature of 1400° C. was 54,500 psi. This compares to an average flexural strength (at 1400° C.) of only 40,900 psi for similarly prepared specimens which did not have the oxidation treatment.

EXAMPLE XXI: Increased Strength

To determine if a higher temperature oxidation treatment could

TABLE I

EXAMPLE NO.	MOLE FRACTION OF Si_3N_4	MOLAR RATIO OF MgO/SiO_2	FLEXURAL STRENGTH		
			UNOXIDIZED	OXIDIZED	INCREASE
V	0.75	0.09	32,700 psi	58,800 psi	80%
VI	0.75	0.32	37,700	66,000	75
VII	0.75	0.53	40,400	65,100	61
VIII	0.75	1.04	28,800	49,100	70
IX	0.75	2.28	27,000	73,900	174
X	0.83	0.97	41,600	65,600	58
XI	0.83	0.22	51,000	61,000	20
XII	0.83	0.54	48,500	65,500	35
XIII	0.83	1.06	30,600	54,600	78
XIV	0.83	0.29	42,000	50,700	21
XV	0.91	0.29	50,000	70,200	40
XVI	0.91	0.50	49,200	77,000	57
XVII	0.91	0.80	44,500	64,500	45
XVIII	0.91	1.57	27,000	47,400	76
XIX	0.91	2.60	39,000	72,400	86

tion aid, specimens were cut from a ceramic of 0.85 mole fraction Si_3N_4, balance Y_2O_3 and SiO_2, with a molar ratio of Y_2O_3/SiO_2 of 0.5. Some of the specimens were oxidized in an air furnace at 1600° C. for 120 hours. The higher oxidation temperature was used because of the higher melting temperature of the Y_2O_3-containing glass as compared to the MgO-containing glass. The oxidized ceramic (curve IV-b) had a higher compressive creep strength than the unoxidized ceramic (curve IV-a) as shown in FIG. 3.

EXAMPLES V–XIX: Increased Strength

Standard flexural strength tests were run on specimens in the Si_3N_4-SiO_2-MgO system having the composition shown in Table I. The specimens were oxidized together in air at 1400° C. for 300 hours. After oxidation, each specimen was separately surface ground until surface pits (formed to various depths on the materials of different composition) were no longer observed by visual inspection with a binocular microscope. Previous work by one of the coinventors (F. F. Lange, "Reaction of Iron with Si_3N_4 Materials to Produce Surface Pitting", Journal of The American Ceramic Society, Vol. 61, No. 5-6, May-June, 1978) has shown that large pits form during the oxidation of many (but no all) Si_3N_4 ceramic compositions. These pits are responsible for the degradation in flexural strength previously reported for commercial Si_3N_4 ceramics fabricated with MgO and subjected to long term oxidation.

be used to reduce the treatment time, flexural test specimens from the NC-132 billet were prepared as described for Example XX except that the oxidation temperature was increased from 1400° C. to 1500° C. The average flexural strength (at 1400° C.) of specimens oxidized at 1500° C. for 206 hours was 69,900 psi. For specimens oxidized at 1500° C. for 306 hours it was 82,000 psi. These strengths compare to an average flexural strength (at 1400° C.) of only 40,900 psi for similarly prepared specimens which did not have the oxidation treatments. While the above treatments increased the high temperature strength of the specimens shown, these treatments neither increased nor decreased these same specimens' room temperature strength (i.e., their room temperature strength was within the normal scatter of untreated specimens).

The advantage obtained by the oxidation treatment as shown in the above examples can be utilized during the compounding and fabrication of the ceramic. In normal practice of preparing Si_3N_4 ceramics, the fabricator adds a densification aid in order to form a liquid phase during sintering and densifying. During cooling from fabrication some or all of the liquid solidifies as a glass. This glassy phase reduces the high temperature strength and oxidation resistance of the ceramic. Therefore, the fabricator must strike a compromise between the amount of densification aid added to improve sintering and the strength of the ceramic. The present invention greatly reduces this problem because it provides a

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means for drawing out some of the glassy phase after the ceramic is densified to improve its high temperature strength and oxidation resistance.

According to the invention, a sufficient quantity of densification aid is added to the Si₃N₄ powder to cause rapid densification due to the formation of a liquid, glassy phase during sintering. The mixture of powder is then sintered to form a dense Si₃N₄ ceramic. The ceramic is cooled and the glassy phase is drawn out by the oxidation treatment previously described.

The amount of grinding required after the oxidation treatment depends upon the depth of the pits formed during the oxidation treatment.

What is claimed is:

1. A post-fabrication method of increasing the high temperature strength of a dense, polyphase silicon nitride (Si₃N₄), structural ceramic, comprising the steps of:

    providing a densified Si₃N₄ ceramic having a glassy phase;

    providing silicon dioxide (SiO₂) on the surface of said Si₃N₄ ceramic;

    heating said Si₃N₄ ceramic and said SiO₂ at a temperature sufficient to cause diffusion of impurity and additive cations from said glassy phase into said SiO₂; and

    removing surface pits formed during said heating step.

2. The method as claimed in claim 1, wherein said step of providing SiO₂ comprises heating said Si₃N₄ ceramic in an oxidizing atmosphere, whereby an SiO₂ scale is formed on said Si₃N₄ ceramic by oxidation of said Si₃N₄ ceramic.

3. The method as claimed in claim 1, wherein said step of providing SiO₂ comprises packing said Si₃N₄ ceramic in SiO₂ powder.

4. The method as claimed in claim 1, wherein said Si₃N₄ ceramic comprises an Si-Mg-O-N ceramic and said cations comprise Mg and cations from impurities selected from the group consisting of Ca, Fe, Al, Mn, Na, and K.

5. The method as claimed in claim 1, wherein said Si₃N₄ ceramic having a glassy phase comprises an Si-Ce-O-N ceramic and said cations comprise Ce and cations from impurities selected from the group consisting of Mg, Ca, Fe, Al, Mn, Na and K.

6. The method as claimed in claim 1, wherein said Si₃N₄ ceramic having a glassy phase comprises an Si-Y-O-N ceramic and said cation comprise Y and cations from impurities selected from the group consisting of Mg, Ca, Fe, Al, Mn, Na and K impurities.

7. The method as claimed in claim 1, wherein said Si₃N₄ ceramic having a glassy phase comprises an Si-Al-O-N ceramic and said cation comprises Al and cations from impurities selected from the group consisting of Mg, Ca, Fe, Mn, Na, and K impurities.

8. A method of fabricating an improved silicon nitride (Si₃N₄), structural ceramic, comprising the steps of:

    providing a mixture of Si₃N₄ powder and a sufficient quantity of a densification aid to cause rapid densification due to the formation of a liquid glassy phase during sintering;

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    sintering said mixture to form a dense Si₃N₄ ceramic;

    providing silicon dioxide (SiO₂) on the surface of said Si₃N₄ ceramic;

    heating said Si₃N₄ ceramic and said SiO₂ at a temperature sufficient to cause diffusion of impurities and additive cations from silicates in said glassy phase into said SiO₂; and

    grinding said Si₃N₄ ceramic to a depth sufficient to remove surface pits formed during said heating step.

9. The method as claimed in claim 8, wherein said densification aid comprises a glassy, phase-forming material containing SiO₂ and an element selected from the group consisting of Mg, Ce, Y, Nd, Be, Al, and La.

10. A method of increasing the high temperature strength of a densified, polyphase Si-Mg-O-N, structural ceramic, comprising the steps of:

    providing said Si-Mg-O-N ceramic;

    providing SiO₂ on the surface of said ceramic;

    heating said ceramic at a temperature sufficient to cause diffusion of Mg out of said ceramic and into said SiO₂; and

    grinding said Si-Mg-O-N ceramic to a depth sufficient to remove surface pits formed during said heating step.

11. A method of increasing the high temperature strength of a densified, polyphase Si-Ce-O-N, structural ceramic, comprising the steps of:

    providing said Si-Ce-O-N ceramic;

    providing SiO₂ on the surface of said ceramic;

    heating said ceramic at a temperature sufficient to cause diffusion of Ce out of said ceramic and into said SiO₂; and

    removing surface pits formed during said heating step.

12. A method of increasing the high temperature strength of a densified, polyphase Si-Y-O-N, structural ceramic, comprising the steps of:

    providing said Si-Y-O-N ceramic;

    providing SiO₂ on the surface of said ceramic;

    heating said ceramic at a temperature sufficient to cause diffusion of Y out of said ceramic and into said SiO₂; and

    removing surface pits formed during said heating step.

13. A method of increasing the high temperature strength of a densified, polyphase Si-Mg-O-N, structural ceramic, comprising the steps of:

    providing said Si-Mg-O-N ceramic;

    providing SiO₂ on the surface of said ceramic;

    heating said ceramic at a temperature of at least 1400° C. for at least 24 hours; and

    removing surface pits formed during said heating step.

14. A method of increasing the high temperature strength of a densified, polyphase Si-Y-O-N, structural ceramic, comprising the steps of:

    providing said Si-Y-O-N ceramic;

    providing SiO₂ on the surface of said ceramic;

    heating said ceramic at a temperature of at least 1600° C. for at least 24 hours; and

    removing surface pits formed during said heating step.

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